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PEG-Mediated Catalyst-Free Expeditious Synthesis of Functionalized Benzene/Biaryl and Fluoren-9-one Derivatives from Activated Acetylenes and 1,3-Diones

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ABSTRACT. Poly(ethylene glycol) (PEG) has been used as a sustainable, non-volatile, and environmentally friendly reaction solvent for the synthesis of functionalized benzene/biaryl and fluoren-9-one derivatives from activated acetylenes and 1,3-diones at 100 °C. No additional solvent and catalyst are required.

Key words: Biaryl, PEG, 1,3-Diones, Fluoren-9-one

INTRODUCTION

As useful compounds in organic chemistry and natural product chemistry, polysubstituted benzenes play important roles in medicinal chemistry.[1] Biaryls are beneficial as components in new organic materials like electroluminescent conjugated polymers,[2] semiconductors, and liquid crystals.[3] The quest to develop efficient and versatile methods for the synthesis of substituted benzenes and biaryls has been a perennial theme in organic synthesis. The Friedel-Crafts reaction[4] and the *ortho*-metallation strategy[5] can be used for introducing substituents into the benzene ring. The Reppe reaction,[6] the Vollhardt protocol,[7,8] and the Bergman cyclization[9] have hold many promises for the synthesis of substituted benzenes.

Fluoren-9-ones are an important class of carbocycle because of their significant role in pharmaceutical applications,[10] as photosensitizers,[11] and their use as the key intermediates in organic synthesis.[12] A number of fluoren-9- one natural products, including dengibsin, dengibsinin, and dendroflorin, have recently been reported to occur in the Asiatic orchid *Dendrobium gibsonii* Lindley (*Fig.* 1).[13]

Tilorone, (2,7-bis[2-(diethylamino)ethoxy]-9*H*-fluoren-9-one, *Fig.* 2), was the first low-molecular weight IFN-inducer orally effective in vivo against some DNA and RNA viruses.[14,15]

Carbapenem L-742,728 is a 9*H*-fluoren-9-one derivative and has been reported as an anti-Methicillin-Resistant *Staphylococcus Aureus* (MRSA) agent (*Fig.* 2).[16]

Recently, PEG has been found to be an interesting solvent system. The important difference between using PEG and other neoteric solvents are that all the toxicological properties, the short- and long-term hazards, and the biodegradability, etc., are established and known. The application of PEG as a reaction medium is highly beneficial as the system remains neutral, which helps in maintaining a wide variety of functional groups unchanged that

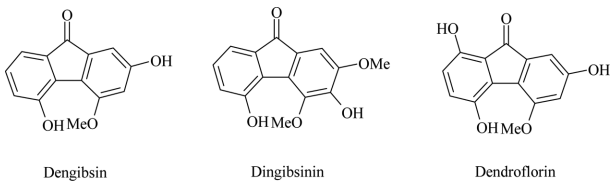


***Fig.* 1.** Structure of some fluoren-9-one natural products.

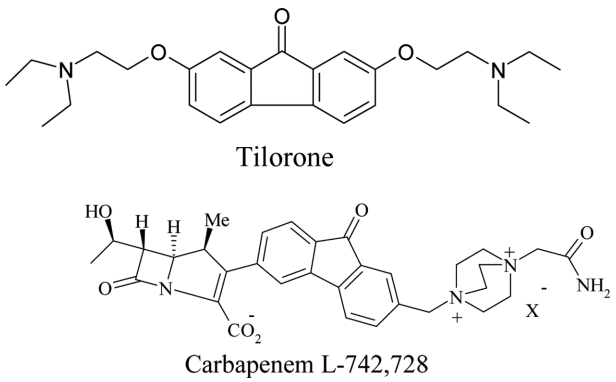


***Fig.* 2.** Structure of some synthesized fluorenone derivatives.

is either acid or base susceptible.[17]

Recently, the synthesis of polysubstituted benzene derivatives using ethyl propiolate with β-dicarbonyl moieties in the presence of DMAP as the catalyst has been reported by Xue et al..[18]

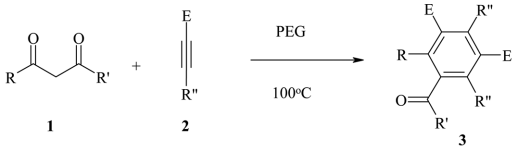
To the best of our knowledge, there is no report of a catalyst-free benzannulation of acetylenic esters with 1,3-dicarbonyl compounds. Based on these findings and as a part of our study on the development of new routes to benzene derivatives,[19] in this paper we report a simple synthesis of functionalized benzene/biaryl and fluoren-9-one systems. Thus, reaction of activated acetylenes with acyclic 1,3-diones and 1,3-indandione in polyethylene glycol (PEG) leads to the corresponding benzene/biaryl and fluoren-9-one derivatives respectively.

RESULTS AND DISCUSSION

The reaction of acyclic 1,3-diones (**1**) and activated acetylenes (**2**) proceeded smoothly in PEG-400 at 100 ºC and was complete within 12 h (*Scheme* 1).

Different solvents, such as methanol, ethanol, acetonitrile, tetrahydrofuran (THF) and PEG-400 were explored. The results are summarized in *Table* 1.

As it can be seen from *Table* 1, the best results were obtained by heating the reaction mixture in PEG-400 at 100 ºC which yielded product **3a** in high yield (*Table* 1, entry 1). Encouraged by this success, we investigated the scope of the reaction of activated acetylenic compounds with acyclic 1,3-diones in PEG-400 at 100 ºC which led to highly polysubstituted benzene/biaryl systems **(3a-g)** in 68-87% yields. It was found that high yield was observed when the reaction was stirred at 100 ºC for 12 h; prolonging the reaction time resulted in no obvious effect on the reaction yield.



1 **2** **3**

3	R	R'	R"	E	Isolated yield(%)
a	Ph	Ph	CO_2Me	CO_2Me	87
b	Ph	Ph	CO_2Et	CO_2Et	84
c	Ph	Ph	H	CO_2Me	81
d	Ph	Ph	H	CO_2Et	79
e	Me	Me	H	CO_2Me	75
f	Me	Me	CO_2Me	CO_2Me	70
g	Me	Me	CO_2Et	CO_2Et	68

***Scheme* 1.** Reaction of acyclic 1,3-diones with activated acetylenes in PEG-400.

The ^{1}H-NMR and ^{13}C-NMR spectra of the crude product clearly indicated the formation of tetramethyl 6-benzoylbiphenyl-2,3,4,5-tetracarboxylate (**3a**) in 87% yield. The reaction was found to be compatible with other acyclic 1,3-diones leading to functionalized benzene/biaryl derivatives in good yields (*Scheme* 1).

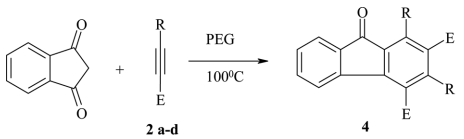
The structures of compounds **3a-3g** were deduced from their IR, ^{1}H-NMR and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum of **3a** exhibited 4 singlets of the H-atoms of the methoxy (3.48, 3.64, 3.92, and 3.93 ppm), alongside characteristic multiplets of the H-atoms of the two phenyl groups. The ^{1}H-decoupled ^{13}C-NMR spectrum of **3a** showed 23 distinct resonances, which further confirmed the proposed structure. The ^{1}H-NMR and ^{13}C-NMR spectra of **3b-3g** were similar to those for **3a** except for the ester moieties, which exhibited characteristic resonances in the appropriate regions of the spectra.

The reaction of cyclic 1,3-diones such as 1,3-cyclohexanedione, dimedone and 1,3-indandione with activated acetylenic compounds in PEG-400 also was investigated. It was found that the reaction of 1,3-indandione with activated acetylenes proceeds smoothly to produce 9*H*-fluoren-9-one derivatives. The reaction was not carried out by the other said cyclic 1,3-diones. Thus the reaction of 1,3-indandione and activated acetylenes in PEG-400 at 100 ºC led to alkyl 9-oxo-9*H*-fluorene-carboxylates (**4a-d**) in good yields (*Scheme* 2).

The structures of compounds **4a-4d** were assigned based on their IR, ^{1}H NMR and ^{13}C NMR spectral data. For example, the ^{1}H NMR spectrum of **4a** exhibited four singlets for the methoxy protons at δ = 3.89, 3.91, 4.02 and

***Table* 1.** Synthetic results of **3a** under different reactions conditions

Isolated Yield (%)	Time/h	Temp/ºC	Solvent	Entry
87	12	100	PEG-400	1
-	18	Reflux	Methanol	2
-	18	Reflux	Ethanol	3
-	18	Reflux	Dichloromethane	4
-	18	Reflux	Acetonitrile	5



4	R	E	Isolated yield(%)
a	CO_2Me	CO_2Me	88
b	CO_2Et	CO_2Et	85
c	H	CO_2Me	83
d	H	CO_2Et	80

***Scheme* 2.** Reaction of 1,3-indandione with activated acetylenes in PEG-400 at 100 ºC.

4.04 ppm, together with characteristic signals for the aromatic moiety. In the ^{13}C NMR spectrum, the signals corresponding to the ester carbonyl groups of **4a** were observed at δ = 165.0, 165.9, 166.4 and 166.5 ppm. The mass spectrum of **4a** displayed the molecular ion peak at m/z = 412. The ^{1}H and ^{13}C NMR spectra of **4b-4d** were similar to those of **4a** except for the alkyl moieties, which exhibited characteristic resonances in appropriate regions of the spectrum. The abovementioned reactions in PEG run in the absence catalyst and products obtained in good yields. It seems the high viscosity of PEG can increase the contact surface between the reagents and generate the adequate position for the reactions to take place.

Although the mechanistic details of the formation of compounds **3** and **4** are not known, a plausible rationalization is proposed in *Scheme* 3. Presumably, the intermediate **7**, which is formed from the successive reaction of dibenzoylmethane and two molecules of DMAD, can undergo enolization and proton transfer reaction to afford the hexatriene **8**. Intermediate **8** can undergo 6π-electrocyclic reaction followed by loss of water to give **3a**.

In conclusion, we have revealed an efficient synthesis of functionalized benzene/biaryl and 9*H*-fluoren-9-one derivatives from a free catalyzed condensation of activated acetylenes and 1,3-diones in PEG. This frees catalyst process created polysubstituted benzene with some electron-withdrawing groups, which was difficult to construct by other conventional methods. This finding prompted us to explore the feasibility of the construction of polysubstituted benzenes based on utilization of readily available acetylenic esters and 1,3-dicarbonyl moieties. Simple mixing of the starting materials and the potential diversity of this type of reaction are the advantages of this procedure.

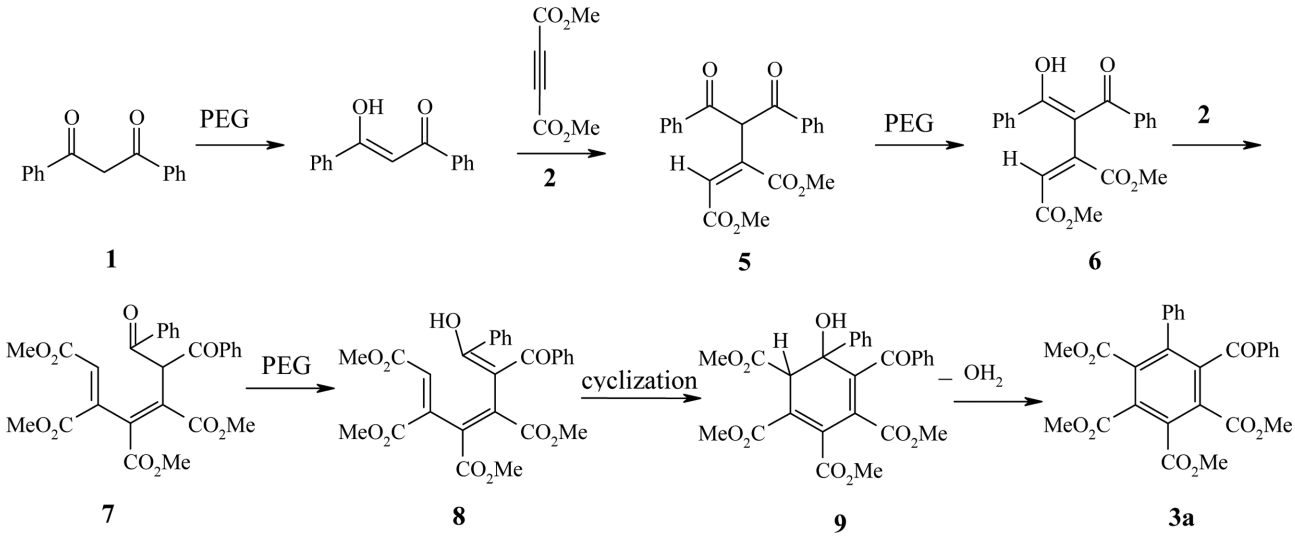
EXPERIMENTAL

General

Acetylenic esters, 1,3-diones and PEG-400 were obtained from *Merck* and were used without further purification. M.p.: *Electrothermal-9100* apparatus. IR spectra (KBr, cm^{-1}): *Shimadzu IR-460* spectrometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker DRX-300 Avance* instrument; in $CDCl_3$ at 500 and 75 MHz, resp.; δ in ppm, *J* in Hz. MS: *Finnigan-MAT-8430* mass spectrometer, at 70 eV; in *m/z* (rel. %). Elemental analyses (C, H, N): *Heraeus CHN-O-Rapid* analyzer.

Typical Procedure for the Preparation of 3(a-g)

To a stirred solution of 1,3-dicarbonyle (2 mmol) was added activated acetylene (4 mmol) in PEG-400 (2 g). The reaction mixture was heated at 100 ºC. After completion



***Scheme* 3.** Proposed mechanism for the formation of compound **3a**.

of the reaction (12 h), as indicated by TLC (AcOEt/hexane, 2:1), the reaction mixture was cooled to r.t. and the product was extracted with Et_2O (3 × 4 mL). The solvent was removed under reduced pressure to afford pure **3(a-g)**.

Tetramethyl 6-benzoylbiphenyl-2,3,4,5-tetracarboxylate (3a)

Yield 0.43 g (87%). White crystals, m.p: 123-125 °C IR (KBr): [1734, 1726, 1720, 1710, 1682 (C=O)], 1282 (C-O). ^{1}H-NMR: 3.48 (3H, s, MeO), 3.64 (3H, s, MeO), 3.92 (3H, s, MeO), 3.93 (3H, s, MeO), 7.00-7.06 (2H, m, CH), 7.13-7.17 (3H, m, CH), 7.40 (1H, t, ^3J = 7.7 Hz, CH), 7.47 (2H, d, ^3J = 7.6 Hz, CH). ^{13}C-NMR: 53.0 (MeO), 53.4 (MeO), 53.7 (MeO), 53.8 (MeO), 128.3 (2 CH), 128.6 (2 CH), 128.8 (CH), 129.4 (2 CH), 131.0 (C), 132.1 (2 CH) 133.6 (C), 133.7 (C), 135.4 (C), 137.1 (C), 137.2 (C), 140.9 (C), 141.1 (C), 142.8 (C), 165.9 (COO), 166.0 (COO), 166.8 (COO), 167.1 (COO), 195.5 (C=O). EI-MS: 490 (M^+, 6), 459 (4), 258 (18), 167 (55), 149 (100), 105 (42), 77 (28), 59 (15). Anal. calc for $C_{27}H_{22}O_9$ (490.45): C 66.12, H 4.52; found: C 66.3, H 4.6.

Tetraethyl 6-benzoylbiphenyl-2,3,4,5-tetracarboxylate (3b)

Yield 0.46 g (84%). White crystals, m.p: 117-118 °C. IR (KBr): [1736, 1725, 1721, 1719, 1718 (C=O)], 1257 (C-O). ^{1}H-NMR: 0.87 (3H, d, ^3J = 7.1 Hz, Me), 0.95 (3H, d, ^3J = 7.1 Hz, Me), 1.31 (3H, d, ^3J = 7.1 Hz, Me), 1.36 (3H, d, ^3J = 7.1 Hz, Me), 3.90 (2H, q, ^3J = 7.1 Hz, CH_2O), 4.29-4.37 (6H, m, 3 CH_2O), 6.95-6.99 (2H, m, CH), 7.05-7.10 (3H, m, CH), 7.20 (2H, t, ^3J = 7.7 Hz, CH), 7.37 (1H, t, ^3J = 7.3 Hz, CH) 7.45 (2H, d, ^3J = 7.7 Hz, CH). ^{13}C-NMR: 13.5 (Me), 13.7 (Me), 14.1 (Me), 14.2 (Me), 62.1 (CH_2O), 62.2 (CH_2O), 62.8 (CH_2O), 62.9 (CH_2O), 128.2 (2 CH), 128.5 (2 CH), 128.7 (CH), 129.5 (2 CH), 131.7 (C), 132.1 (2 CH), 133.2 (C), 133.6 (CH), 135.6 (C), 136.9 (C), 137.2 (C), 137.3 (C), 140.2 (C), 143.1(C), 165.4 (COO), 165.7 (COO), 166.3 (COO), 166.7 (COO), 195.5 (C=O). EI-MS: 546 (M^+, 3), 501 (5), 149 (100), 105 (40), 77 (31), 73 (15). Anal. calc for $C_{31}H_{30}O_9$ (546.56): C 68.12, H 5.53; found: C 68.0, H 5.43.

Dimethyl 6-benzoylbiphenyl-2,4-dicarboxylate (3c)

Yield 0.30 g (81%). White powder. M.p. 123-125 °C. IR (KBr): [1734, 1724, 1720 (C=O)], 1266 (C-O). ^{1}H-NMR: 3.36 (3H, s, MeO), 3.98 (3H, s, MeO), 7.12-7.17 (4H, m, CH), 7.27-7.32 (3H, m, CH), 7.44 (1H, t, ^3J = 7.6 Hz, CH), 7.54 (2H, t, ^3J = 7.6 Hz, CH), 8.24 (1H, d, ^4J = 1.7 Hz, CH), 8.61 (1H, d, ^4J = 1.7 Hz, CH). ^{13}C-NMR: 52.7 (MeO), 53.0 (MeO), 128.2 (2 CH), 128.4 (CH), 128.6 (2 CH), 129.2 (2 CH), 129.6 (C), 130.1 (2 CH), 131.4 (CH), 132.2 (CH), 133.4 (C), 133.7 (CH), 137.2 (C), 137.5 (C), 141.9 (C), 144.8 (C), 165.8 (COO), 168.0 (COO), 197.1 (C=O). EI-MS: 374 (M^+, 4), 341 (6), 151 (100), 105 (41), 77 (34), 59 (15). Anal. calc for $C_{23}H_{18}O_5$ (374.39): C 73.79, H 4.85; found: C 73.6, H 4.7.

Diethyl 6-benzoylbiphenyl-2,4-dicarboxylate (3d)

Yield 0.32 g (79%). White powder. M.p. 110-112 °C. IR (KBr): [1733, 1728, 1722 (C=O)], 1260 (C-O). ^{1}H-NMR: 0.82 (3H, d, ^3J = 7.1 Hz, Me), 1.12 (3H, d, ^3J = 7.1 Hz, Me), 3.92 (2H, q, ^3J = 7.1 Hz, CH_2O), 4.08 (2H, q, ^3J = 7.1 Hz, CH_2O), 7.09-7.14 (4H, m, CH), 7.24-7.30 (3H, m, CH), 7.38 (1H, t, ^3J = 7.7 Hz, CH), 7.51 (1H, d, ^3J = 7.7 Hz, CH), 8.15 (1H, d, ^4J = 1.8 Hz, CH), 8.52 (1H, d, ^4J = 1.8 Hz, CH). ^{13}C-NMR: 13.6 (Me), 13.7 (Me), 62.1 (CH_2O), 62.6 (CH_2O), 128.4 (2 CH), 128.5 (CH), 128.7 (2 CH), 129.0 (2 CH), 129.3 (C), 130.6 (CH), 130.7 (2 CH), 131.4 (CH), 132.8 (C), 133.2 (CH), 135.1 (C), 136.6 (C), 139.2 (C), 143.3 (C), 164.9 (COO), 166.3 (COO), 196.2 (C=O). EI-MS: 402 (M^+, 6), 347 (5), 151 (100), 105 (52), 77 (40), 73 (45). Anal. calc for $C_{25}H_{22}O_5$ (402.44): C 74.61, H 5.51; found: C 74.5, H 5.6.

Dimethyl 5-acetyl-4-methylisophthalate (3e)

Yield 0.19 g (75%). Yellow oil. IR (KBr): [1726, 1722, 1718 (C=O)], 1260 (C-O). ^{1}H-NMR: 2.06 (3H, s, Me), 2.60 (3H, s, Me), 3.92 (3H, s, MeO), 3.94 (3H, s, MeO), 8.24 (1H, d, ^4J = 1.6 Hz, CH), 8.47 (1H, d, ^4J = 1.6 Hz, CH). ^{13}C-NMR: 21.0 (Me), 30.1 (Me), 52.8 (MeO), 53.0 (MeO), 128.0 (C), 131.4 (CH), 133.3 (CH), 133.6 (C), 142.1 (C), 142.9 (C), 165.9 (COO), 167.7 (COO), 202.6 (C=O). EI-MS: 250 (M^+, 3), 219 (8), 207 (42), 59 (50), 43 (100). Anal. calc for $C_{13}H_{14}O_5$ (250.25): C 62.39, H 5.64; found: C 62.5, H 5.8.

Tetramethyl 5-acetyl-6-methyl-1,2,34-benzene tetra carboxylate (3f)

Yield 0.25 g (70%). Yellow oil. IR (KBr): [1733, 1730, 1720, 1686, 1680 (C=O)], 1282 (C-O). ^{1}H-NMR: 2.32 (3H, s, Me) 2.53 (3H, s, COMe), 3.85 (3H, s, MeO), 3.87 (3H, s, MeO), 3.90 (3H, s, MeO), 3.91 (3H, s, MeO). ^{13}C-NMR: 16.4 (CH_3), 31.8 ($COCH_3$), 53.0 (MeO), 53.2 (MeO), 53.4 (MeO), 53.9 (MeO), 129.3 (C), 133.4 (C), 138.0 (C), 140.0 (C), 143.1 (C), 146.2 (C), 165.3 (COO), 165.6 (COO), 166.1 (COO), 167.1 (COO), 203.5 (C=O). Anal. calc for $C_{17}H_{18}O_9$ (366.30): C 55.70, H 4.95; found: C 55.67, H 4.96.

Tetraethyl 5-acetyl-6-methyl-1,2,34-benzene tetra carboxylate (3g)

Yield 0.28 g (68%). Yellow oil. IR (KBr): [1733, 1730, 1720, 1688, 1684 (C=O)], 1280 (C–O). ^{1}H-NMR: 1.27-1.40 (12H, m, Me) 2.30 (3H, s, Me), 2.52 (3H, s, COMe), 4.28-4.34 (8H, m, OCH_2) .^{13}C-NMR: 13.7 (CH_3), 13.8 (CH_3), 13.9 (CH_3), 14.4 (CH_3), 16.4 (CH_3), 31.8 ($COCH_3$), 62.1

(OCH_2), (MeO), 62.4 (OCH_2), (MeO), 62.8 (OCH_2), (MeO), 63.2 (OCH_2), 128.9 (C), 133.5 (C), 139.0 (C), 142.0 (C), 143.1 (C), 146.5 (C), 165.2 (COO), 165.4 (COO), 166.0 (COO), 167.1 (COO), 203.3 (C=O). Anal. calc for $C_{21}H_{26}O_9$ (422.42): C 59.71, H 6.20; found: C 59.68, H 6.18.

Typical procedure for the preparation of 4(a-d)

To a stirred solution of 1,3-indandione (0.3 g, 2 mmol) was added activated acetylene (4 mmol) in PEG (2 g). The reaction mixture was heated at 100 ºC. After completion of the reaction (12 h), as indicated by TLC (AcOEt/hexane, 2:1), the reaction mixture was cooled to r.t. and the product was extracted with Et_2O (3 × 4 mL). The solvent was removed under reduced pressure to afford pure **4(a-d)**.

Tetramethyl 9-oxo-9H-fluorene-1,2,3,4-tetracarboxylate (4a)

Yield 0.36 g (88%). Yellow oil. IR (KBr): [1735, 1728, 1723, 1721, 1715 (C=O)], 1256 (C-O). ^{1}H-NMR: 3.89 (3H, s, MeO), 3.91 (3H, s, MeO), 4.02 (3H, s, MeO), 4.04 (3H, s, MeO), 7.45 (1H, t, ^3J = 7.3 Hz, CH), 7.52-7.64 (2H, m, CH), 7.74 (1H, d, ^3J = 7.4 Hz, CH). ^{13}C-NMR: 53.6 (MeO), 53.7 (MeO), 53.8 (MeO), 62.0 (MeO), 124.4 (CH), 125.4 (CH), 128.2 (C), 130.0 (C), 131.7 (CH), 132.8 (C) 133.1 (C), 134.6 (C), 136.1 (CH), 138.5 (C), 140.9 (C), 144.4 (C), 165.0 (COO), 165.9 (COO), 166.4 (COO), 166.5 (COO), 189.4 (C=O). EI-MS: 412 (M^+, 7), 381 (10), 149 (100), 105 (50), 77 (44), 71 (56), 59 (42). Anal. calc for $C_{21}H_{16}O_9$ (412.34): C 61.17, H 3.91; found: C 61.4, H 4.0.

Tetraethyl 9-oxo-9H-fluorene-1,2,3,4-tetracarboxylate (4b)

Yield 0.40 g (85%). Yellow oil. IR (KBr): [1734, 1727, 1723, 1720, 1719 (C=O)], 1262 (C-O). ^{1}H-NMR: 0.90 (3H, d, ^3J = 7.1 Hz, Me), 1.02 (3H, d, ^3J = 7.1 Hz, Me), 1.32 (3H, d, ^3J = 7.1 Hz, Me), 1.34 (3H, d, ^3J = 7.1 Hz, Me), 4.12 (2H, q, ^3J = 7.1 Hz, CH_2O), 4.25-4.32 (4H, m, CH_2O), 4.36 (2H, q, ^3J = 7.0 Hz, CH_2O), 7.47 (1H, t, ^3J = 7.6 Hz, CH), 7.53-7.63 (2H, m, CH), 7.70 (1H, d, ^3J = 7.6 Hz, CH). ^{13}C-NMR: 13.7 (Me), 14.0 (Me), 14.1 (Me), 14.2 (Me), 62.3 (CH_2O), 62.5 (CH_2O), 62.8 (CH_2O), 63.1 (CH_2O), 124.3 (CH), 125.2 (CH), 128.4 (C), 130.1 (C), 131.8 (CH), 133.0 (C) 133.2 (C), 134.8 (C), 136.3 (CH), 138.6 (C), 140.9 (C), 145.3 (C), 165.1 (COO), 166.0 (COO), 167.5 (COO), 167.9 (COO), 188.8 (C=O). EI-MS: 468 (M^+, 5), 413 (15), 149 (100), 105 (53), 77 (54), 73 (48), 71 (49). Anal. calc for $C_{25}H_{24}O_9$ (468.45): C 64.10, H 5.16; found: C 64.3, H 5.2.

Dimethyl 9-oxo-9H-fluorene-2,4-dicarboxylate (4c)

Yield 0.25 g (83%). Light brown powder. M.p. 165-167 ºC. IR (KBr): [1734, 1726, 1723 (C=O)], 1264 (C-O). ^{1}H-NMR: 3.46 (3H, s, MeO), 3.82 (3H, s, MeO), 7.44 (1H, t, ^3J = 7.5 Hz, CH), 7.50-7.61 (2H, m, CH), 7.68 (1H, d, ^3J = 7.5 Hz, CH), 8.30 (1H, d, ^4J = 1.7 Hz, CH), 8.71 (1H, d, ^4J = 1.7 Hz, CH). ^{13}C-NMR: 51.3 (MeO), 52.5 (MeO), 123.3 (CH), 124.2 (CH), 126.2 (CH), 129.2 (C), 130.9 (CH), 132.1 (CH) 133.6 (C), 135.1 (C), 136.6 (CH), 138.2 (C), 140.3 (C), 145.7 (C), 164.8 (COO), 166.7 (COO), 187.4 (C=O). EI-MS: 296 (M^+, 6), 265 (15), 151 (100), 105 (40), 77 (41), 59 (52). Anal. calc for $C_{17}H_{12}O_5$ (296.27): C 68.92, H 4.08; found: C 67.9, H 4.1.

Diethyl 9-oxo-9H-fluorene-2,4-dicarboxylate (4d)

Yield 0.26 g (80%). Light brown powder. Mp: 148-150 ºC. IR (KBr): [1734, 1726, 1724 1613 (C=O)], 1261 (C-O). ^{1}H-NMR: 0.84 (3H, d, ^3J = 7.1 Hz, Me), 1.13 (3H, d, ^3J = 7.1 Hz, Me), 4.06 (2H, q, ^3J = 7.1 Hz, CH_2O), 4.27 (2H, q, ^3J = 7.1 Hz, CH_2O), 7.41 (1H, t, ^3J = 7.6 Hz, CH), 7.48-7.57 (2 H, m, CH), 7.61 (1H, d, ^3J = 7.6 Hz, CH), 8.25 (1H, d, ^4J = 1.6 Hz, CH), 8.69 (1H, d, ^4J = 1.6 Hz, CH). ^{13}C-NMR: 13.3 (Me), 14.3 (Me), 62.8 (CH_2O), 63.1 (CH_2O), 124.2 (CH), 125.1 (CH), 125.9 (CH), 127.8 (C), 129.9 (CH), 131.7 (CH) 132.8 (C), 133.6 (C), 135.8 (CH), 137.9 (C), 138.1 (C), 144.1 (C), 164.6 (COO), 165.9 (COO), 190.6 (C=O). EI-MS: 324 (M^+, 5), 279 (10), 151 (100), 105 (41), 77 (44), 73 (46). Anal. calc for $C_{19}H_{16}O_5$ (324.33): C 70.36, H 4.97; found: C 70.4, H 5.1.

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